Field-Induced Quasiparticle Excitation in $Ca(Al_{0.5}Si_{0.5})_2$: Evidence for Unconventional Superconductivity

Sogo KUROIWA[1], Hiroyuki TAKAGIWA[1], Maki YAMAZAWA[1], Jun AKIMITSU[1], Kazuki OHISHI[2], Akihiro KODA[2], Wataru HIGEMOTO[2] and Ryosuke KADONO[2]*

[1] *Department of Physics, Aoyama-Gakuin University, Fuchinobe, 5-10-1, Sagamihara, Kanagawa, 229-8558*
[2] *Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK), Tsukuba, Ibaraki 305-0801*

The temperature (T) and magnetic field (H) dependence of the magnetic penetration depth, $\lambda(T, H)$, in $Ca(Al_{0.5}Si_{0.5})_2$ exhibits significant deviation from that expected for conventional BCS superconductors. In particular, it is inferred from a field dependence of $\lambda(H)$ ($\propto H$) at 2.0 K that the quasiparticle excitation is strongly enhanced by the Doppler shift. This suggests that the superconducting order parameter in $Ca(Al_{0.5}Si_{0.5})_2$ is characterized by a small energy scale $\Delta_S/k_B \leq 2$ K originating either from anisotropy or multi-gap structure.

Since the discovery of binary intermetallic compound superconductor MgB_2 (T_c=39 K),[1] the origin of pair correlation leading to such high critical temperature has been drawing much interest. Up to now, a majority of experiments as well as theories suggests that the pair correlation is mediated by a strong electron-phonon interaction, where the relatively high T_c is explained by the light mass of the two-dimensional honeycomb layer formed by B atoms. The two-dimensional feature is also preferable for the strong electron-phonon interaction, and thereby the AlB_2-type crystal structure common to MgB_2 is currently attracting attention as a possible basis for developing new superconductors.

In binary silicides, $ThSi_2$,[2] USi_2,[3] and several rare-earth metal disilicides have the AlB_2-type structure. β-$ThSi_2$ is known to be a superconductor with a critical temperature T_c=2.41 K.[4] Above 16 GPa, $CaSi_2$ takes a AlB_2-like structure, and it becomes superconducting with T_c=14 K.[5] Recently, a new ternary silicide, $Sr(Ga,Si)_2$, which also has the AlB_2-type structure, was reported to be a superconductor with T_c=3.4 K,[6] stimulating active investigation of analogous compounds. In this class of materials, ternary silicide $Ca(Al_{0.5}Si_{0.5})_2$ has the highest critical temperature T_c=7.7 K.[7] It is reported on this compound that the behavior of electron-heat capacity deviates from that of the BCS-type, and that the effect of hydrostatic pressure on T_c is positive.[8] Unfortunately, despite various experiments so far, there is very little known on the structure of superconducting order parameter in $Ca(Al_{0.5}Si_{0.5})_2$.

In this paper, we report the quasiparticle excitation in the flux line lattice (FLL) state of $Ca(Al_{0.5}Si_{0.5})_2$ studied by muon spin rotation (μSR). The magnetic penetration depth λ, which reflects the quasiparticle excitation, can be determined by μSR due to the inhomogeneity of the magnetic field distribution in the FLL state. We show temperature (T) and magnetic field (H) dependence of λ in polycrystalline sample of $Ca(Al_{0.5}Si_{0.5})_2$. Our result indicates that λ is proportional to T^3 at low temperature, and that it exhibits a steep increase with almost linear

dependence on the applied magnetic field. These findings strongly suggest that $Ca(Al_{0.5}Si_{0.5})_2$ has an anisotropic order parameter or a multi-gap structure with a band having a small gap energy, which is qualitatively similar to the case in MgB_2.

The samples were prepared by arc melting method with a stoichiometric mixture of Ca (99.9%), Al (99.99%), and Si (99.999%) (in 1:1:1 composition) under an Ar atmosphere. The structure of polycrystalline sample was examined using a powder x-ray diffraction technique. Diffraction signal from $Ca(Al_{0.5}Si_{0.5})_2$ phase was observed as a main contribution besides those from a small amount of impurity phases. Magnetic susceptibility and electrical resistivity measurements were performed with the SQUID magnetometer (MPMSR2) and the PPMS system (Quantum Design Co. Ltd.). The residual resistivity ratio was estimated to be 2.85.

Figure 1 shows the temperature dependence of magnetic susceptibility at 10 Oe. The solid triangles and circles show data obtained in zero-field cooling (ZFC) and in field cooling (FC), respectively. In FC, a Meissner effect can be seen below 7.7 K. The inset of Figure 1 shows the
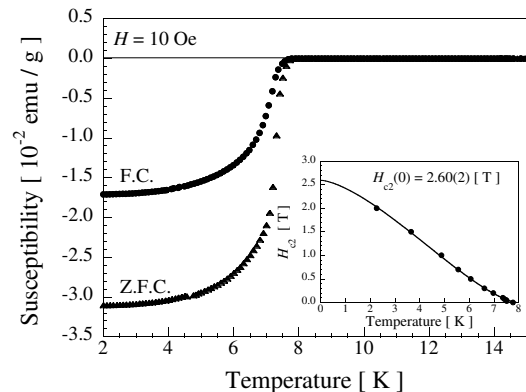

Fig. 1. Temperature dependence of magnetic susceptibility at 10 Oe. The inset shows the upper critical field versus temperature.

temperature dependence of the upper critical field (H_{c2}) which was estimated from the temperature dependence of electrical resistivity at respective magnetic fields. The solid line is the result of fitting analysis by the following equation from a local-paring theory,

$$H_{c2}(T) = H_{c2}(0)(1 - \tau^{3/2})^{3/2}, \qquad (1)$$

where $\tau = T/T_c$, which yields $H_{c2}(0) = 2.60(2)$ T.

The μSR experiment was performed on the M15 beam line at the Tri-University Meson Facility (TRIUMF, Canada) which provides a muon beam with a momentum of 29MeV/c. The specimen having a dimension of about 7×7 mm^2 was mounted on sample holder and placed in a cryostat. The sample was field-cooled at every magnetic field points to minimize the effect of flux pinning. The temperature and magnetic field dependence of transverse field (TF-) μSR spectrum was obtained at $H = 0.05$ T and $T = 2.0$ K (=$0.26T_c$), respectively. Since the muon stops randomly on the length scale of the FLL, the muon spin precession signal $\hat{P}(t)$ provides a random sampling of the internal field distribution $B(\hat{r})$

$$\hat{P}(t) \equiv P_x(t) + iP_y(t) = \int_{-\infty}^{\infty} n(B) \exp(i\gamma_\mu Bt + \phi)dB, \quad (2)$$

$$n(B) = \langle \delta(B(\hat{r}) - B) \rangle_r, \qquad (3)$$

where γ_μ is the muon gyromagnetic ratio (= 2π 135.53 MHz/T), ϕ is the initial phase of rotation, and $n(B)$ is the spectral density for the muon spin precession signal determined by the local magnetic field distribution. These equations indicate that the real amplitude of the Fourier transformed muon spin precession signal corresponds to the local field distribution $n(B)$. The London penetration depth in the FLL state is related to the second moment of the field distribution $\langle(\Delta B)^2\rangle$, which is reflected in the μSR line shape.[9] For polycrystalline samples, the Gaussian distribution of local field is a good approximation,

$$\hat{P}(t) \simeq \exp(-\sigma^2 t^2/2)\exp(i\gamma_\mu Ht), \qquad (4)$$

$$\sigma = \gamma_\mu \sqrt{\langle(\Delta B)^2\rangle}. \qquad (5)$$

For the ideal triangular FLL with isotropic effective carrier mass m^*, λ is given by the following relation,[9–11]

$$\sigma[\mu s^{-1}] = 4.83 \times 10^4 (1-h)[1 + 3.9(1-h)^2]^{1/2}\lambda^{-2}[nm]. \qquad (6)$$

where $h = H/H_{c2}(T)$, and λ is given by the following relation of superconductive carrier density $n_s(T, H)$

$$\lambda^2 = \frac{m^* c^2}{4\pi n_s(T, H)e^2} \qquad (7)$$

It should be noted that the reduction of σ with increasing field described by Eq. (6) is due to the stronger overlap of $B(\hat{r})$ around vortices at higher fields while λ is a constant. The reduction of $n_s(T, H)$ due to the quasiparticle excitation leads to the enhancement of λ, which causes further reduction of σ from that expected from Eq. (6).

Figure 2 shows the fast Fourier transforms (FFT) spectrum of muon spin precession signal in Ca(Al$_{0.5}$Si$_{0.5}$)$_2$ for several magnetic fields at 2.0 K, where the real amplitude of FFT corresponds to the internal field distribution

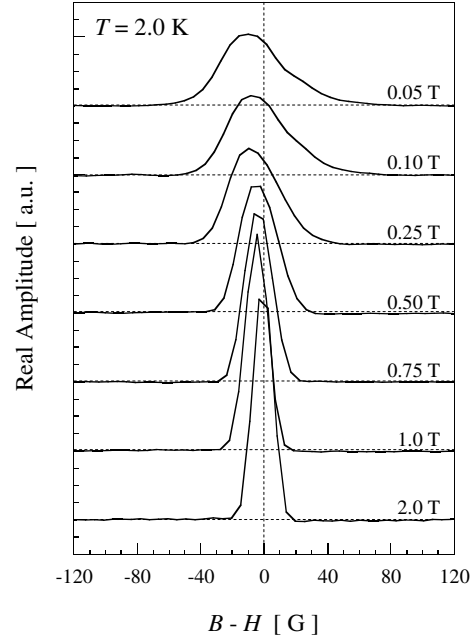Fig. 2. Fast Fourier transform of μSR spectra in Ca(Al$_{0.5}$Si$_{0.5}$)$_2$ at 2.0 K under several applied magnetic fields.

$n(B)$ in the FLL state convoluted with additional damping due to small random field from nuclear moments. As most explicit in FFT spectrum at 0.05 T, the line shape is characterized by the shift of peak to a lower field and also associated broadening of linewidth due to the formation of FLL.

Considering possible contribution from muons stopping in the normal part of the specimen, we adopted two components with the following empirical form in analyzing the μSR time spectra,

$$A\hat{P}(t) = \sum_{i=1}^{2} A_i \exp\left(-\frac{\sigma_i^2 t^2}{2}\right)\exp(\gamma_\mu H_i t + \phi_i) \qquad (8)$$

where the index i refers to the components of superconducting ($i = 1$) and normal ($i = 2$) domains, A is the total positron decay asymmetry with A_i being the partial asymmetry, σ_i is the muon spin relaxation rate, H_i is the central frequency, ϕ_i is the initial phase for respective components. The superconducting volume fraction (= $A_1/(A_1 + A_2)$) was obtained to be $\simeq 0.95$.

The temperature dependence of σ_1 ($\propto n_s$) is shown in Figure 3. In the region below T_c where the FLL is formed, σ_1 increases with decreasing temperature. According to the empirical two-fluid model (which is a good approximation of the BCS theory), the following relation is expected to hold,

$$\sigma_1(T) = \sigma_1(0)[1 - \tau^4] \propto n_s(T) \propto \lambda^{-2}(T). \qquad (9)$$

Solid line is the result of fitting analysis by a similar formula with an arbitrary power,

$$\sigma_1(T) = \sigma_1(0)[1 - \tau^\beta], \qquad (10)$$

whch yields $\beta = 2.73$ and $T_c = 7.53(1)$ K when both β and T_c are assumed to be free parameters. The result also means that the deviation of λ,

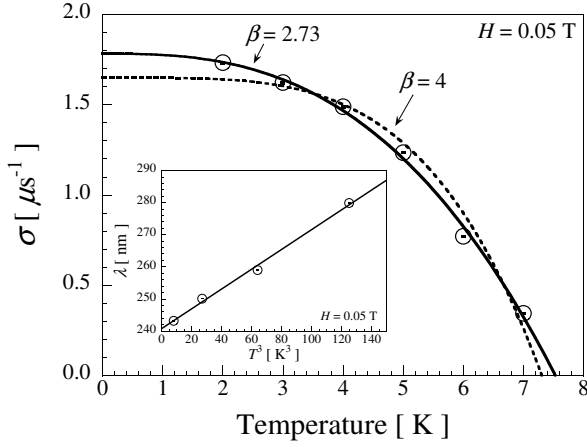$$\delta\lambda = \lambda(T) - \lambda(0), \qquad (11)$$

Fig. 3.　Temperature dependence of the Gaussian relaxation rate σ_1 at 0.05 T. The solid curve is a fitting result with $\sigma_1(T) = \sigma(0)[1 - (T/T_c)^\beta]$, while the dashed curve corresponds to the case $\beta = 4$. Inset: λ plotted against T^3.
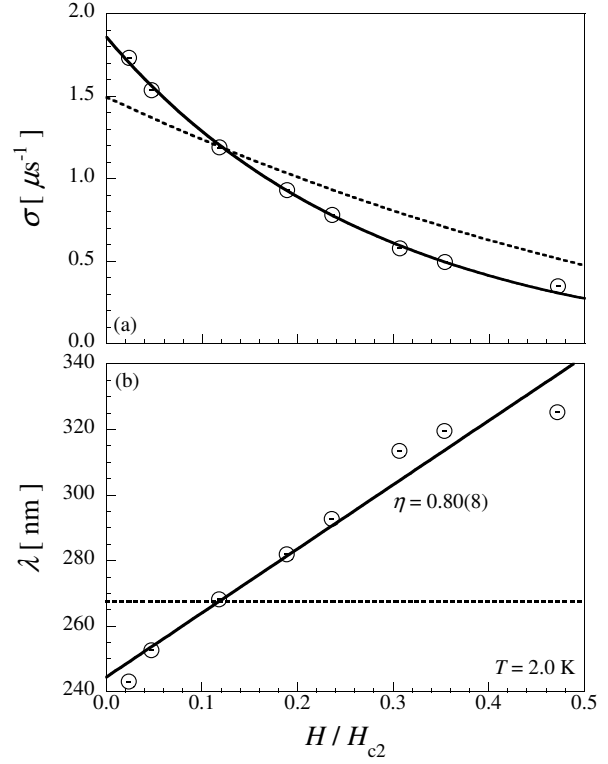

Fig. 4.　Magnetic field dependence of the Gaussian relaxation rate σ_1 (a), and penetration depth λ (b) at 2.0 K. Solid curves are fitting result with $\lambda(h) = \lambda(0)[1 + \eta h]$, and the dashed curves correspond to $\eta = 0$.

exhibits a tendency predicted for the case of line nodes (d-wave pairing) with some disorder (i.e., dirty limit, where $\delta\lambda \propto T^2$).[12] Since the gap energy $\Delta(T) \simeq \Delta_0(1 - \tau^4)$ is predicted to be least dependent on temperature for $\tau \leq 0.4$ in the BCS model, the observed deviation of β from 4 suggests the presence of excess quasiparticle excitation. This leads to the possibility that the order parameter has an anisotropic strutcure, where the excess quasiparticles are induced at the vicinity of nodes ($|\Delta_{\hat{k}}|/k_B \leq 2$ K). Another possibility may be that, assuming a multi-gap structure with Δ_S being one of the smallest gap energy, the excess quasiparticles are due to the thermal activation over Δ_S ($\Delta_S/k_B \leq 2$ K) ; unfortunately, the absence of data below 2.0 K did not allow us to perform the reliable fitting analysis using a two-gap model.[15]

The presence of an energy scale smaller than that for the single BCS-gap energy Δ_0 is further supported by the magnetic field dependence of λ. As shown in Fig. 4a, $\sigma(h)$ decreases with increasing field much steeply than expected by Eq. (6). Accordingly, λ exhibits a strong field dependence, where λ increases almost linearly with h (see Fig. 4b). This is similar to the case of NbSe$_2$[16] and YNi$_2$B$_2$C[17] which exhibit characters specific to anisotropic order parameters in spite of the suggested s-wave symmetry, or to that of MgB$_2$[18] having a two-gap structure. Solid curves in Fig. 4 is the result of fitting by the following linear relation,

$$\lambda(h) = \lambda(0)[1 + \eta h], \tag{12}$$

where η is a dimension-less parameter which represents the strength of pair breaking effect. Fitting yields $\eta = 0.80(8)$ (with $H_{c2} = 2.12(2)$ T determined by Eq. (1)) which is comparable with that in NbSe$_2$, YNi$_2$B$_2$C and MgB$_2$ (i.e., $\eta = 1.61$, 0.97, and 1.27, respectively).

In the FLL state, the quasiparticle energy spectrum around the vortex cores is shifted by an amount $\varepsilon = \hat{p}\cdot\hat{v}_s$ due to the semiclassical Doppler shift, where $\hat{p}$ is the quasiparticle momentum ($\simeq m^*\hat{v}_F$), and $\hat{v}_s$ is the velocity of supercurrent. Since the density of state (DOS),

$N(E)$, for anisotropic order parameters takes a non-zero value for an energy $E > 0$, quasiparticles can be excited by the Doppler shift outside of the vortex cores with a population proportional to $N(\varepsilon)$, leading to the enhancement of λ.[19] The magnitude of η represents the degree for the increase of DOS for quasiparticles, which must be roughly proportional to the phase volume of the Fermi surface where the Doppler shift exceeds the gap energy ($\varepsilon > |\Delta_{\hat{k}}|$). It also follows that the effect depends on the direction of $\hat{v}_s$ (and hence that of the external field $\mathbf{H}$ relative to the order parameter) in a single crystalline specimen. According to Volovik, the quasiparticle density of state for anisotropic order parameter is

$$N_{\text{deloc}}(0) \simeq N_F K \xi_{\text{GL}}^2 \sqrt{h} \equiv N_F g(h), \tag{13}$$

$$K \propto \int_{|\Delta_{\hat{k}}|<\varepsilon} |\Delta_{\hat{k}}| d\mathbf{k}, \tag{14}$$

where N_F is the DOS for the normal state and K is a constant on the order of unity.[19] It is important to note that K is proportional to the phase volume of the low excitation energy in $\Delta_{\hat{k}}$, thereby carrying information on the degree of anisotropy for $\Delta_{\hat{k}}$; the factor $h^{1/2}$ comes from the inter-vortex distance ($\propto h^{-1/2}$) multiplied by the number of vortices ($\propto h$). The superfluid density at a given field is then

$$n_s(h) \simeq n_s(0)[1 - g(h)], \tag{15}$$

which is directly reflected in the magnetic penetration depth through Eq. (7). Therefore, as a mean approxima-

tion, we have

$$\lambda(h) = \frac{\lambda(0)}{\sqrt{1 - g(h)}} \sim \lambda(0)[1 + cK\xi_{GL}^2 h], \qquad (16)$$

where $c \simeq 1.5$ for $0 < h < 0.5$.[20] Thus, the comparison between Eqs. (12) and (16) yields

$$\eta \simeq cK\xi_{GL}^2, \qquad (17)$$

indicating that the slope η reflects the phase volume of the Fermi surface where $|\Delta_{\hat{k}}| < \varepsilon$. The situation in the case of multi-gap state is similar when $\Delta_S \leq k_B T$. For example in the two-gap model,[15] using the relative weight, $1 - x$, of the quasiparticle DOS for the smaller gap Δ_S, we have

$$K \propto 1 - x. \qquad (18)$$

Since the Doppler shift is far smaller than the gap energy in usual situation for the isotropic gap, no such enhancement is expected for the conventional s-wave pairing (i.e., $\eta \ll 1$ for $|\Delta_0|$, $|\Delta_S| \gg k_B T$). For example in $Y(Ni_{0.8}Pt_{0.2})_2B_2C$, which behaves as a conventional BCS superconductor with an isotropic gap, it is reported that $\eta \simeq 0$.[21] This is in good contrast with the case of YNi_2B_2C in which an anisotropic gap (two-gap state with point nodes) is strongly suggested by other experiments.[22, 23] On the other hand, a stronger magnetic field dependence is predicted for the case of d-wave pairing due to the relatively large value of K. Typical examples of the d-wave pairing are found in high-T_c cuprates, in which η is reported to be 5-6.6 for YBCO.[24] The comparison of those earlier results with our result suggests that $Ca(Al_{0.5}Si_{0.5})_2$ has an anisotropic order parameter comparable to that of YNi_2B_2C or a multi-gap order parameter in which one of those has a small gap energy ($|\Delta_S|/k_B \leq 2$ K) as found in MgB_2.

Unfortunately, our results were obtained using polycrystalline samples, which makes it difficult to deduce λ by analyzing data using the well-defined microscopic model. Early experiments on high quality single crystal sample of $Ca(Al_{0.5}Si_{0.5})_2$ have reported that the upper critical field has an anomalous angular dependence which deviates from the Ginsburg-Landau anisotropic mass model.[25] Moreover, very recent report suggests that the crystal structure has clear fivefold and sixfold superlattice. Therefore, we are preparing high quality single crystals of $Ca(Al_{0.5}Si_{0.5})_2$ for further μSR study of this compound in more detail.

In conclusion, We have performed μSR experiments on polycrystalline $Ca(Al_{0.5}Si_{0.5})_2$ to elucidate the structure of superconducting order parameter. We found that $n_s(t)$ exhibits a considerable deviation from that expected for the BCS prediction, and that $\lambda(h)$ exhibits significant increase with applied magnetic field. These results strongly suggest the presence of unconventional order parameter in $Ca(Al_{0.5}Si_{0.5})_2$.

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